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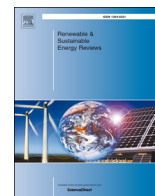
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The use of gasification solid products as catalysts for tar reforming

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ABSTRACT

The presence of tars in syngas is a major technological constraint for upscaling biomass gasification to produce heat, power, and other value-added chemicals such as biofuels. At the same time, the solid remains from biomass gasification i.e. char and ashes, have capabilities to catalyse the reforming of gasification tars. This work presents a comprehensive analysis of the relevance of gasification chars and ashes as catalysts for tar reforming. A description of the solid products from biomass gasification, their formation, chemical characteristics and potential applications is given. Additionally, a review of the state of the art of the uses of regular char, activated carbon and ashes as a catalyst for tar reforming is presented. Further, kinetics reported in literature, and the homogeneous and heterogeneous mechanisms for tar reforming over char are discussed and explained. From reviewing literature it was found that activated chars exhibit the best reforming capabilities, followed by regular char and ashes. Knowing the role of the interactions between the char and the tars is a key factor for optimization of char catalysts. Ultimately, this work provides guidance for understanding the uses of biomass solids as catalysts for tar reforming, and aid in future research to increase the economic feasibility of biomass gasification.

1. Introduction

The growing resource demands and environmental concerns have brought great attention towards renewable energies such as biomass energy. Biomass energy has advantages over fossil fuels such as CO₂ neutrality and renewability [1], and research in the area has led to the development of processes like biomass pyrolysis and gasification to obtain fuels and satisfy the world's energetic demands as efficiently as possible [2–5].

Biomass gasification involves the thermal transformation of the components of biomass (cellulose, hemicellulose and lignin) into a gas fuel called syngas (consisting of CO and H₂), and other side products like tars, which are hydrocarbons with higher molecular weight than benzene [6], and solids (constituted by chars and ashes). The proportion of the products varies depending on the feedstock and the operation conditions [7–10].

Syngas can be used for power generation in internal combustion engines, upgraded by processes such as but not limited to Fischer-Tropsch synthesis, oxosynthesis and methanation, or other advanced applications, such as using the H₂ in fuel cells [5,11]. However, to prevent environmental compromises, it is indispensable to remove

pollutants from the syngas before its use. Tar contents from biomass gasification can be as high as 75–100 g/Nm³ [12]. Unfortunately, the maximum tar loads in syngas are much lower, in the ranges of 0.05 g/Nm³, 0.005 g/Nm³, 0.001 g/Nm³, 0.001 g/Nm³ and 0.1 ppmv for gas engines, gas turbines, fuel cells, Fischer-Tropsch synthesis and methanol synthesis, respectively [13,14]. As tars have been acknowledged as particularly problematic, physical, thermal and catalytic treatment technologies have been proposed to remove or decompose the tars and tested to varying degrees of success. Physical treatments such as wet scrubbing are relatively simple but less than optimal due to losses in the syngas heating value [14]. Thermal treatments are effective but energetically constrained by the exceedingly high temperatures of more than 1000 °C that are required for effective tar destruction [15]. Finally, while catalytic treatments tackle most of the problems associated to physical and thermal treatments and appear promising, they are not without faults. The catalysts used during clean up are deactivated either because the tars deposit as coke on the surface of the catalyst, or because the temperatures or other operating conditions cause structural collapse [14]. Constant deactivation means constant catalyst replacement is necessary, which in turn leads to increases in the cost of the technology.

Abbreviations: AAEM, Alkaline and Alkaline Earth Metals; AC, Activated Char; BET, Brunauer-Emmet-Teller; ER, Equivalence ratio; HACA: Hydrogen-Abstraction/Carbon Addition; LHV, Lower Heating Value; N/A, Not applicable; N/R, Not reported; PAH, Polyaromatic Hydrocarbon; ppmv, Parts per million, volume; SEM, Scanning Electron Microscope; SBR, Steam/biomass ratio; SSA, Specific Surface Area

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Table 1
Ultimate and proximate analysis of biomass chars. ER: Equivalence Ratio, SBR: Steam/biomass ratio, N/R: Not reported, N/A: Not applicable.

Feedstock type	Ultimate analysis results % composition					Proximate analysis % composition			Reactor type and scale	Gasification agent	ER or SBR	Formation temperature (°C)	Ref
	C	H	O	N	S	Fixed carbon	Volatile matter	Ashes					
Mesquite woodchips	84.5	1.0	13.7	0.5	0.3	86.1	3.5	9.8	Commercial downdraft gasifier	Air	N/R	N/R	[17]
Corn cob	78.5	1.2	10.4	0.5	0.1	86.7	3.9	8.6	Commercial downdraft gasifier	Air	0.8	N/R	[49]
Rice husk	9.0	0.5	90.2	< 0.2	0.1	4.0	7.1	86.9	Laboratory fluidised-bed gasifier	Air	0.2	850	[28]
Pine sawdust	76.1	1.0	8.1	2.5	0.3	81.1	5.5	10.4	Pilot scale unknown type gasifier	Steam	0.4	850	[50]
Pine wood	86.3	2.3	6.2	0.1	0.0	79.7	15.2	5.0	Laboratory fixed-bed pyrolyzer	N/A	N/A	800	[51]
Furniture sawdust	90.1	1.2	2.4	0.2	6.1	75.4	16.6	8.0	Laboratory fixed-bed pyrolyzer	N/A	N/A	850	[43]
Rice straw	91.2	1.0	1.6	0.8	5.6	43.6	23.0	33.5	Laboratory fixed-bed pyrolyzer	N/A	N/A	850	[43]
Sewage sludge	18.1	0.5	79.5	1.1	0.8	12.0	3.2	84.8	Laboratory fixed-bed pyrolyzer	N/A	N/A	N/R	[25]
Pine sawdust	78.8	1.8	19.4	0.0	0.0	94.2	3.6	2.2	Laboratory fixed-bed pyrolyzer	N/A	N/A	850	[52]
Wood chips	85.0	3.5	11.6	0.2	0.0	79.2	19.5	1.3	Laboratory fixed-bed pyrolyzer	N/A	N/A	500	[53]
Wood chips	85.9	1.4	9.2	0.3	0.0	87.1	11.2	1.7	Laboratory fixed-bed pyrolyzer	N/A	N/A	800	[53]
Rice husk	48.0	3.8	47.6	0.6	0.0	7.8	5.4	86.8	Laboratory fixed-bed pyrolyzer	N/A	N/A	700	[54]
Wood	85.9	3.3	10.9	0.0	0.0	73.9	24.1	2.0	Laboratory fixed-bed pyrolyzer	N/A	N/A	500	[44]
Paddy straw	86.3	3.1	7.4	3.2	0.0	41.1	6.5	52.4	Laboratory fixed-bed pyrolyzer	N/A	N/A	500	[44]
Palm kernel shell	87.8	2.9	8.2	1.1	0.0	80.8	12.3	6.9	Laboratory fixed-bed pyrolyzer	N/A	N/A	500	[44]
Coconut	91.4	0.3	7.4	0.9	0.0	91.6	2.6	5.8	Not reported	N/A	N/A	N/R	[25]

On the other hand, chars and ashes, which are byproducts from gasification, need appropriate waste handling. The amount of char produced during conventional gasification normally varies between 1 and 30 g per Nm³ of syngas, while the amount of ashes varies between 0.21 and 26 g per Nm³ of syngas [11]. Moreover and importantly, different applications for the produced gases have different maximum allowances for solid particulates: gas engines require particulate contents below 50 mg/Nm³, gas turbines require less than 15 mg/Nm³ and fuel synthesis requires a strict amount of solids of less than 0.02 mg/Nm³ [11]. As the amount of produced solids is not negligible, some works have been dedicated to exploring different alternatives for the use of the solid chars and ashes produced from biomass gasification. Commonly, chars are taken to secondary gasification. Other alternatives for char use are as precursor for activated char (AC), fertilizers or catalysts for decomposition of NO_x (Nitrogen Oxides) precursors, production of synthesis gas using CO₂ and tar reforming, etcetera [16–25]. On the side of ashes, uses are as fertilizers, construction materials, and more recently, as catalysts for some processes such as tar reforming, oxidation of nitrogen species and bio-oil upgrading [26–33]. Char can have a performance on par with commercial and expensive catalysts when used for tar reforming [34]. Ashes have not achieved the same success as chars, but still contribute to reducing the syngas tar contents [23]. Therefore, the use of solids from gasification as catalysts for tar reforming is a landfill alternative that also presents an opportunity to improve the viability of gasification as a mean for energy production. This mitigates some of the environmental impacts associated to the process, which include but are not limited to impacts associated with energy consumption and waste production.

In contrast to the abundance of literature related to the biomass gasification process and syngas clean up, there are only a few studies dedicated to the uses of the resulting solids in specific ways. For example, the use of biomass char as soil conditioner was reviewed by Sohi et al. [21], and the uses of biomass char as a catalyst for biodiesel production through transesterification, hydrolysis and dehydration were reviewed by Konwar et al. [35] and Cao et al. [36]. The review by Ahmaruzzaman [37] elaborates on some uses of biomass ashes such as adsorbent and additives for construction materials. None of the mentioned works explain the tar reforming capabilities of biomass gasification chars and ashes in detail. In this regard, an adequate compilation of relevant findings represents a powerful tool to guide future research with the ultimate goal of increasing the feasibility of biomass gasification as a clean energy source.

This work summarizes the advances in the usage of solids from biomass gasification as catalysts for tar reforming. First, the characteristics of chars and ashes from biomass gasification, including a description of their formation process, are given. This provides an adequate background to relate the formation conditions, potential usage, and the relevance of char and ashes as catalysts. A following subsection elaborates briefly on other applications which are unrelated to catalysis; a detailed description of these is beyond the scope of this manuscript. Afterwards, an analysis of the homogeneous and heterogeneous mechanisms for tar reforming using char as a catalyst is conferred, followed by an overview of reported kinetics collected from experiments using char and activated char as catalysts. Subsequently, advances on the usage of regular char and activated char both as a catalyst and as a catalyst support for tar reforming are present. Analogous to the char, the next subsection covers the usage of ashes both as a catalyst and catalyst support for tar reforming. Concluding remarks to provide a guideline for future research are given last, recommending what could be sought to improve the use of char based catalysts for syngas tar removal, with the goal of augmenting the economic attractiveness of biomass gasification.

2. Overview of gasification solid products

2.1. Characteristics

Biomass gasification solid products are composed either by char, a carbonaceous solid with a characteristic graphitic microstructure, or ashes, which constitute the non-volatile inorganic species in biomass (90–95% weight of the inorganic species in biomass) and a fraction of the carbon (10–60% weight) [38–41]. Further, ashes are categorized as fly ash or bottom ash depending on the floatability of the particles: fly ashes are capable of mixing with flue gas, while bottom ashes suspend to the ground [42].

Table 1 enlists the results from the ultimate and proximate analyses of different chars produced and reported in several works. The fixed carbon, volatile matter and ash contents are highly variable and depend majorly on the feedstock, followed by the formation conditions. For example, the rice husk char reported in [28] was obtained from a gasifier and has, in weight percentage, 4.0% fixed carbon, 7.1% volatile matter and 86.9% ashes. On the other hand, the rice straw char from pyrolysis reported in [43] has a 43.6% carbon content, 23.0% volatile matter and 33.5% ash content. This occurs due to rice husk being naturally high in ash contents. The same occurs with the paddy straw reported in [44], which had a naturally high amount of silica in its composition. For usage as catalyst for tar reforming, the most valuable quality of a biomass solid should be surface area (which is directly related to fixed carbon) [45]. Moreover, as some ashes have a catalytic effect [23], these are another important asset for char-based catalysts. Indeed, it has been demonstrated that chars impregnated with ashes increase their gasification reactivity by several orders of magnitude [46]. Nevertheless, it is important to mention that not all ashes contribute to the activity, as while Ni and Mg contents are known catalyst, Si is an inert species abundantly present in some biomasses [47]. On the side of volatile matter, it has been demonstrated that H-radicals have influence in the char reactivity. Particularly, the radicals contribute to coke growth and inhibit gasification reactions, an undesirable quality for the catalysis of tar reforming reactions [48].

The main sources of the char from biomass gasification are lignin and, to a lesser extent, hemicellulose [55]. The carbon fraction in the solids is amorphous, disordered and contains elemental carbon (50–80% weight), trace inorganics and heavy compounds such as polyaromatic hydrocarbons (PAHs) [56]. The aromatic hydrocarbons and functional groups in char undergo constant evolution during formation process, hence, char does not have a defined chemical structure [57].

Gasification chars exhibit a mesoporous/microporous structure owed to the activating agent that propagates pore enlargement; the proportion of the pore size depends on the char precursor and gasification conditions [17,28,57]. The pore size distribution is important for catalysis, as this directly affects the diffusion of species into the char matrix [58]. Additionally, different acidic and alkaline functional groups such as carboxylic, lactonic, carbonyl, phenolic and phenoxide are found in the pores in the char surface; these, together with structural amorphism, confer high activity for adsorptive/catalytic use in a number of processes, including syngas tar reforming [59,60]. The porosity in the solids can decrease by sintering or coking during operation; in this situation, micro-pores are the first to be fouled. SEM (Scanning Electron Microscope) images of various chars [61–63] are illustrated in Fig. 1. Fig. 1A, B and C are the surfaces of fresh chars, Fig. 1D is fresh activated char, Fig. 1E is fouled char and Fig. 1F is sintered activated char. Some of the lost pores and catalytic activity may be restored under certain conditions. Coke-filled pores can be unblocked by introducing air, N₂ and/or CO₂ [61,64–66], and in the presence of steam, continuous gasification of tars deposited in active sites can occur [34].

Physically, ashes, whose structure is defined during formation, are irregularly shaped particles with varying sizes and porosities. Some

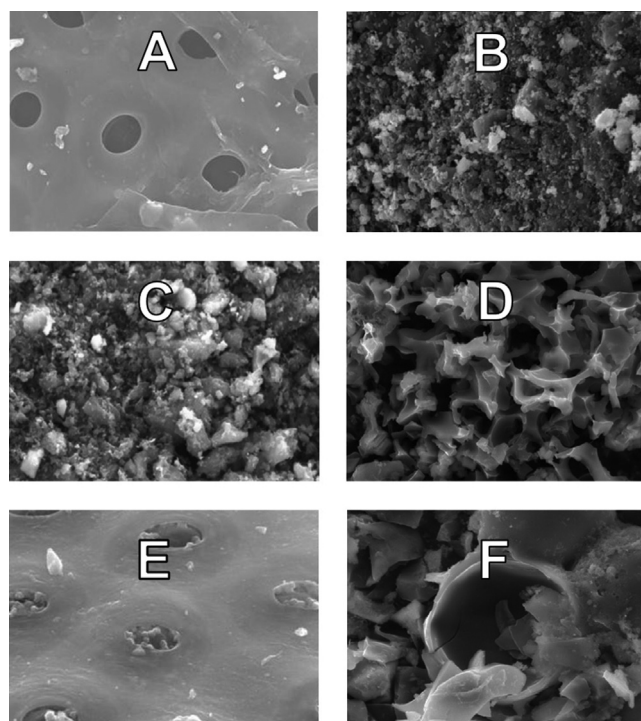


Fig. 1. SEM images of carbon surfaces. Left column corresponds to fresh samples and right column corresponds to used samples. A) is woodchip char, B) and C) are coal char, D) is cornstalk activated char, E) is fouled coal char and F) is fouled cornstalk activated char. A) and E) reprinted from [62], with permission from N. Klinghoffer, “Catalyst properties and catalytic performance of char from biomass gasification”, vol. 51 (40), pp. 13113–13122, 2012. Copyright 2012 American Chemical Society. B) and C) reprinted from [61], Chemical Engineering Journal, vol. 291, F. Di Gregorio et al., “Removal of naphthalene by activated carbons from hot gas”, 244–253, Copyright 2016, with permission from Elsevier. D) and F) reprinted from [63], Journal of Cleaner Production, vol. 143, A. Zubrik et al., “Preparation of chemically activated carbon from waste biomass by single-stage and two-stage pyrolysis”, 643–653, Copyright 2017, with permission from Elsevier.

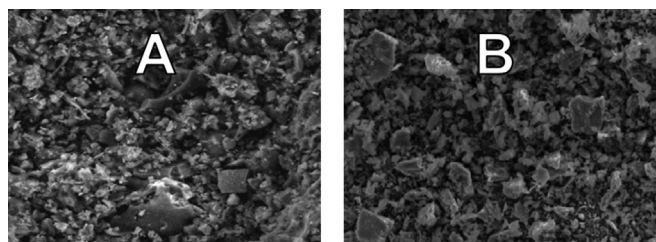


Fig. 2. SEM images of ashes. A) coal powder ash and B) rice husk ash. Fig. 2A) reprinted from [67], Procedia Engineering, vol. 148, A. Herman et al., “Bottom ash characterization and its catalytic potential in biomass gasification”, 432–436, Copyright 2016, with permission from Elsevier. Fig. 2B) reprinted from [68], Fuel, vol. 165, I.J. Fernandes et al., “Characterization of rice husk ash produced during different biomass combustion techniques for energy”, 351–359, Copyright 2016, with permission from Elsevier.

images of ashes from [67] and [68] are found in Fig. 2. In Fig. 2A, it can be observed that the ashes suffered sintering (i.e. the particles look melted and stuck together) during formation, whereas ashes from Fig. 2B do not present the sintering effect that may occur at temperatures as low as 700 °C [69]. Ash sintering depends on the physico-chemical properties of the ash species and is undesirable because this blocks active sites necessary for interaction with the gases during catalysis. With regards to the chemical composition, Fig. 3 presents a scheme of the species commonly found in different biomass ashes

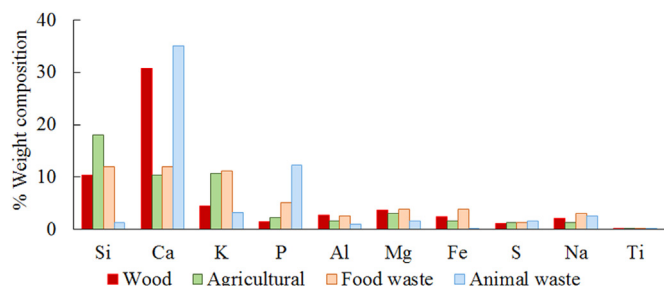


Fig. 3. Average fractions of inorganic species in a range of biomass ashes by type of biomass [31,32,43,47,54,70–74].

[31,32,43,47,54,68,70–74]; from the values in the figure, it can be inferred that the most prevalent inorganic elements in the ashes are Si and Ca. Moreover, it is clear that the inorganic species come in different amounts from different biomasses. Woody biomass is enriched in Ca, Mg and Mn [59,75], straws and grasses are enriched in Cl, K, N, Na, S and Si [75], biomass from husks is often enriched with K, C, Si and P [76] and animal biomass (e.g. chicken litter) is enriched with Ca, P, Al and K [77]. The works by Vassilev et al. [47,59] present an extended description of the composition of biomass and biomass ashes and the reader is encouraged to consult the references if the species distribution in biomass is of interest.

2.2. Formation

Fig. 4 portrays the products of the different biomass conversion technologies. As can be observed, the different technologies yield different products and byproducts, and it is noticeable that char is only considered a byproduct when produced during gasification and not when produced during pyrolysis. This is because during gasification a maxima is expected for the gas phase [11]. In addition to the solids called char, a carbonaceous agglomeration of particles called soot may be produced from secondary reactions such as carbon deposition and tar dehydrogenation [78]. The atmosphere under which the biomass decomposes has a notable impact in the resulting solids. The presence of H₂ inhibits formation of soot from PAHs [15], and under an oxidizing atmosphere, secondary reactions yield gases such as CO instead of soot

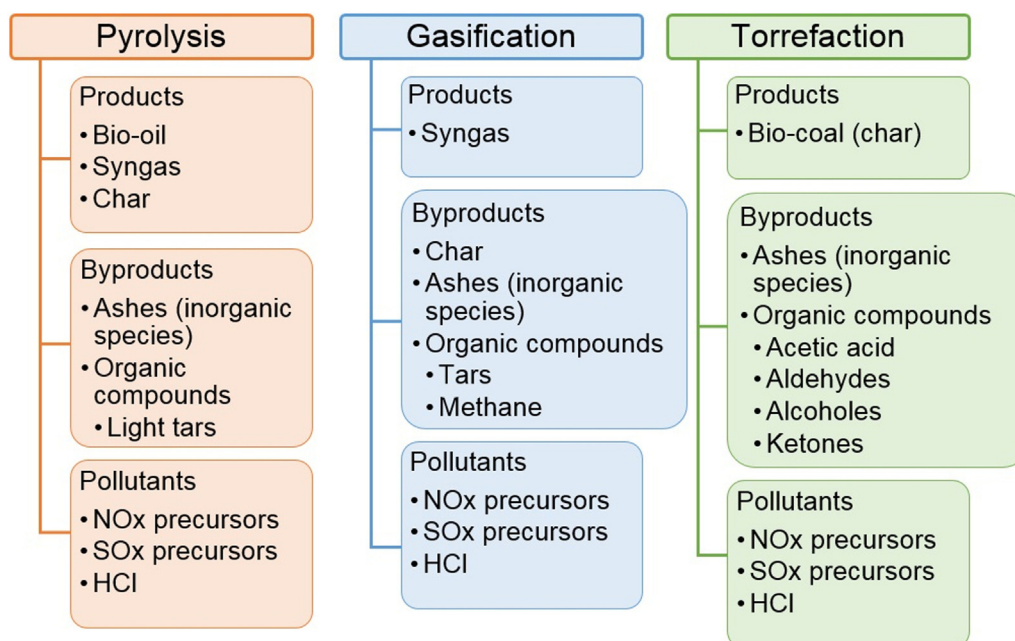


Fig. 4. Thermal biomass conversion technologies and their common products, byproducts and pollutants.

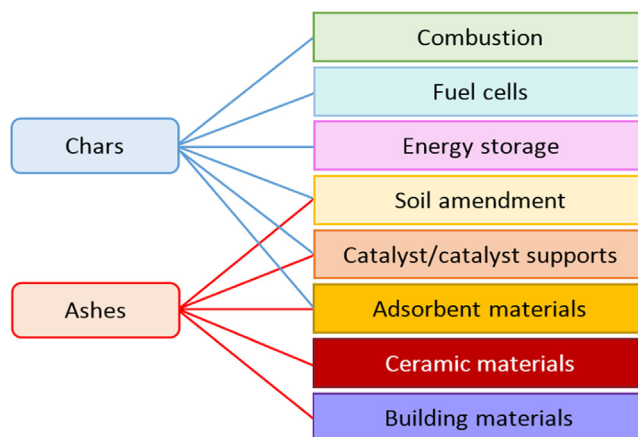


Fig. 5. Uses of biomass gasification chars and ashes.

[80,81]. Moreover, Hernandez et al. [56] demonstrated that the specific surface area (SSA) of char increases with biomass/gasifying agent ratio to a maximum (3.5 in their work), followed by SSA decreases due to structural collapses, soot deposition and inhibition of gasification reactions. O₂ as gasifying agent yields the largest SSA, followed by steam and air [28,43,56].

Formation temperatures and heating rate also have influence on the carbon structure. The carbon percentage is directly affected by temperatures [21], and exceedingly high temperatures may cause burn-off which changes the pore distribution and chemically active sites and favours the formation of ashes [42–44]. The alkalinity of the ashes also depends on temperatures because high temperatures may cause melting [82]. Slow heating contributes to higher char yield, as this allows for internal rearrangement and formation of the carbonaceous structure. The structure of the particles has an effect in the gasification reactivity, where an ordered structure has more reactivity than a disordered one [83].

2.3. Usage

As illustrated in Fig. 5, there are six main applications for gasification chars and five for ashes. The different characteristics of each

solid product suggests different usages [27,59,67,84–87]. Solids with high carbon content (> 60% weight) can be gasified or combusted [1] while solids with an adequate SSA (> 70 m²/g) may be ground and used for preparing AC for adsorption purposes [56,88]. When the ashes in the solids are composed by chemically active species (e.g. alkali species), the ashes in the solids may be more relevant and the solids can be employed either as soil amendment [26] or as precursor for catalyst synthesis [32,89]. Additionally, due to oxygenated functional groups, ashes can be attractive for wastewater treatment because of their alkaline nature, porosity and ion exchange capacity [59]. Other popular uses of ashes are as construction materials, where they replace a fraction of other substances such as limestone and cement [27,37,85].

Additionally, chars with high surface areas have seen novel usages such as fuel for direct carbon fuel cells, anode material for microbial fuel cells and super capacitors, while the advanced uses for ashes are as precursor for ceramic materials [59,90–93].

It is important to note that solids with heavy metal contents are unsuitable for some applications such as soil amendment or fertilization [26,38,94,95]. The use of solids for soil amendment becomes complicated when the inorganic fraction is present in water insoluble phases such as silicates and phosphates [47]. These examples of technical limitations establish a need for alternative uses for chars and ashes. On the other hand, due the constant deactivation during operation, tar reforming catalysts require constant replacement, leading to increases in the process costs. The catalytic capabilities of a substance are determined by its activity, selectivity and stability. In other words, catalysts need to be capable of facilitating reaction paths towards the desired product while at the same time being chemically, thermally and mechanically stable. Hence, properties desirable for a catalyst or a catalyst support are prevalent both in chars and ashes [96]. Chars are specially suitable for employment either as a catalyst or as a support because their overall high porosity, high surface area and their status as a byproduct in a number of processes, making it relatively inexpensive and environmentally friendly. At the same time, ashes often contain alkali and alkaline earth metals (AAEM), which are species present in popular catalysts for tar reforming because of their activity and selectivity [34,67,97]. Therefore, it is clear that the usage of solids from biomass gasification as catalysts represents an alternative to handling them as solid waste.

3. Biomass gasification chars for catalytic tar reforming

Table 2 enunciates the surface area of the solid products from a range of works; it can be seen that chars have a larger surface area than coals. Since heterogeneous catalytic reactions occur on the solid surface, it is intuitive to think of the surface area as a key factor for activity. Alas, conserving the surface area of catalysts during tar reforming is one of the main challenges for tar reforming catalysts, including those based on char [25]. Under appropriate conditions, the coke formed over the char surface can be gasified. However, care needs to be paid to conserve the desired activity when employing char based catalysts, as the char catalyst may be gasified, decreasing the overall tar reforming rate [98].

The char catalytic properties are partially due to the radicals found on the surface [96]. These are oxygen functional groups (O-radicals), responsible for adsorbing polar molecules, and acidic sites, responsible of catalysing the cleavage of C-C and C-H bonds. The reforming activity of the O-radicals is further augmented by the presence of AAEM species [105]. However, under the presence of AAEM species, some factors that otherwise contribute to the catalyst activity may become antagonistic, as for example in [96] it was shown that the catalytic contribution of the mineral species decreases with increasing temperature, as at around 1000 °C the metals accumulate in the surface and block the pores.

Table 2
Surface properties of some chars based catalysts employed in the literature.

Material	Preparation method	BET SSA (m ² /g)	Pore volume (cm ³ /g)	Avg. pore size (nm)	Ref.
Coal	–	3.55	0.02	29.9	[99]
Fe/coal	Impregnation	3.02	0.02	32.8	[99]
Ni-Fe/coal	Impregnation	4.99	0.03	22.8	[99]
Ni-Fe/coal	Impregnation	8.41	0.04	20.6	[99]
Gasifier ash	–	172.36	0.17	3.96	[42]
Zeolite 1	–	424.00	0.22	3.33	[74]
Zeolite 2	–	407.00	0.24	3.69	[74]
Zeolite 3	–	345.00	0.2	3.71	[74]
Coal	–	15.40	0.11	3.00	[100]
Ni/coal	Impregnation	9.00	0.05	3.50	[100]
Ni nitrate/AC carbon	Impregnation	965.00	0.42	8.49	[101]
Ni acetate/AC	Impregnation	945.00	0.40	18.00	[101]
Rice husk char	–	51.99	0.03	2.56	[102]
Ni/rice husk char	Impregnation	183.97	0.12	2.66	[102]
Fe/rice husk char	Impregnation	192.51	0.10	2.15	[102]
Cu/rice husk char	Impregnation	188.68	0.11	2.41	[102]
Mo/char	Impregnation	422.00	0.23	24.20	[103]
Mo/char	Impregnation	362.30	0.20	24.60	[103]
Mo/char	Impregnation	323.40	0.20	25.40	[103]
Mo/char	Impregnation	317.80	0.19	25.70	[103]
Mo/char	Impregnation	247.10	0.17	29.90	[103]
Brown coal AC	–	990.74	0.53	21.24	[104]

3.1. Description of tar reforming mechanism over char/activated char based catalysts

Two chemical pathways have been proposed for the decomposition of tars using char catalysts, referred to in this work as the homogeneous and heterogeneous reforming mechanisms. The scheme in Fig. 6 presents an overview of the homogenous and heterogeneous interactions between common model tar compounds (toluene, benzene and naphthalene) and the char surface during reforming. Additionally, the

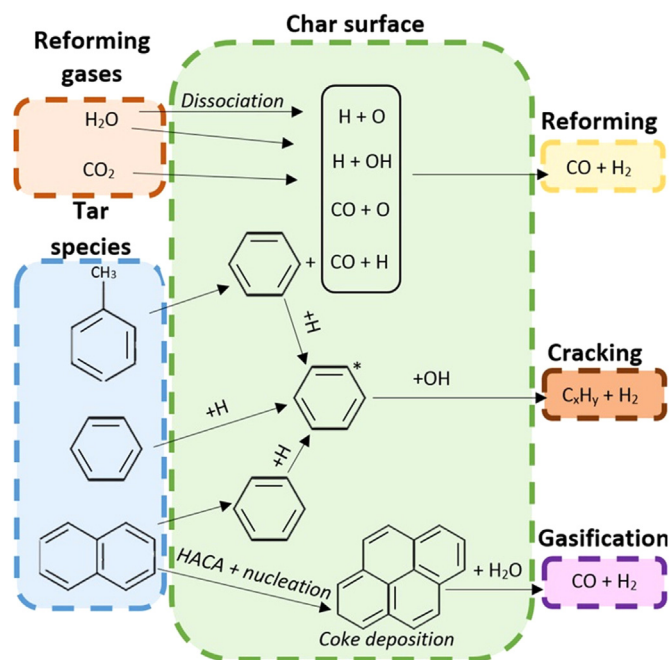


Fig. 6. Simplified mechanism of the heterogeneous tar reforming reactions with a char based catalyst.

Table 3
Reactions involved in the degradation of tar compounds.

Carbon formation	$C_n H_m \rightarrow nC + \left(\frac{m}{2}\right)H_2$	(1)
Thermal cracking	$x C_n H_m \rightarrow y C_i H_j + k H_2$	(2)
Hydrocracking	$C_n H_m + \left(\frac{4n - m}{2}\right)H_2 \rightarrow nCH_4$	(3)
Steam reforming (1)	$C_n H_m + 2nH_2O \rightarrow nCO_2 + \left(\frac{m}{2} + 2n\right)H_2$	(4)
Steam reforming (2)	$C_n H_m + nH_2O \rightarrow nCO + \left(n + \frac{m}{2}\right)H_2$	(5)
Dry reforming	$C_n H_m + nCO_2 \rightarrow 2nCO + \left(\frac{m}{2}\right)H_2$	(6)
Water-gas shift	$CO + H_2O \rightleftharpoons CO_2 + H_2$	(7)
Steam gasification	$C_{(s)} + H_2O \rightarrow H_2 + CO$	(8)
Boudouard reaction	$2CO \rightleftharpoons CO_2 + C_{(s)}$	(9)

reactions involved in the degradation of tars using char can be found in Table 3. Homogeneous reforming consists on the char surface adsorbing the tar, followed by the tar being reformed over the char surface to yield CO and H₂ [16,106–109]. Heterogeneous reforming consists the deposition of tar on the char surface, followed by coke gasification [25,50,105,110]. As pointed out in [111], PAHs are more prone to coke formation than single ring compounds, thus when a group of tars are lumped together, the heavier PAHs are favoured by heterogeneous reforming while the lighter tars are homogeneously reformed. This makes the reforming mechanism depend on the operation temperatures. At temperatures around 600 °C, tars will consist mostly of phenolic compounds, at around 700 °C alkyl substituted PAHs show prevalence, and at temperatures over 800 °C the predominant species are PAHs. Hence, heterogeneous reforming is favoured by high temperatures [112].

During homogeneous reforming, tars are adsorbed over the char surface and interact with surface functional groups. Besides the functional groups native to the char, the reforming gases and the H₂ found in the syngas can dissociate over the char to form H-, OH- and O-groups [110,113–115]. The tar molecules dissociate over the surface producing radicals by the cleavage of C-C bonds, facilitated by the presence of mineral species in the char matrix [96], and reform either by steam or dry reforming at adequate temperatures (Eqs. 4–6 in Table 3) [106]. An example of this phenomena was reported in [105], where char enriched with K exhibited a decrease of C-C/C-H bonds in the char surface due to interactions with dissociated species for H₂/CO production. The reforming yields can be augmented by the water-gas shift reaction (Eq. (7) in Table 3) and the reverse Boudouard reaction (Eq. (9) in Table 3). On another hand, H₂ inhibits the reforming rate and increases the tar deposition/coking rate (Eq. (1) in Table 3) [15]. The products of the reactions are lighter tars, H₂, CO and coke (Eqs. (1) and (5) from Table 3), and the product distribution varies depending on the reaction conditions. With regards to coke, its formation during homogeneous reforming results from the agglomeration of PAHs in the char surface. An example of coke formation from benzene is depicted in Fig. 7 [114].

Heterogeneous reforming consists in two key steps. First, the tars are adsorbed over the surface active sites and decomposed via the carbon formation reaction (Eq. (1) in Table 3). Above certain temperatures (usually 700 °C), soot precursors from secondary

polymerization reactions start appearing [116,117]. The soot precursors decompose and may form coke, with the amount formed related to the available carbon surface [107]. This occurs because PAHs interact with the H-radicals present on the char surface propagating the coke growth [118], explaining the increased tendency for coke deposition with increasing molecule size. Additional coke may be formed following the HACA (Hydrogen-Abstraction/Carbon-Addition) mechanism, where hydrogen atoms are abstracted from gaseous hydrocarbons and acetylene is repeatedly added to the radical site, resulting in the formation of large hydrocarbons that result in coke [119]. During the second step of the heterogeneous reforming, the carbon deposits reacts with the atmosphere (usually H₂O or CO₂) to produce H₂ and/or CO, via steam gasification or the reverse-Boudouard reaction (Eqs. 8 and 9 in Table 3). Nucleation for additional coke deposits by the HACA mechanism occurs when the gasification reactions are not thermodynamically favoured [98]. This scheme is outlined in Fig. 8, where the evolution of pore blocking across time is seen in Fig. 8a and the coke deposition or gasification is seen in Fig. 8b. As seen in Fig. 8a, coke deposition has a stronger effect in chars with higher microporosity. The micropores are the first to be deactivated, followed by meso and macropores [98]. Coking of micropores limits mass transfer to active sites, reducing the overall catalytic reaction rates. Nevertheless, if particles are small enough, the bulk mass transfer may be the same regardless pore size [120]. On the other hand, as seen in Fig. 8b, if the gasification rate is higher than the carbon formation rate, the catalyst undergoes continuous reforming and regeneration. Contrarily, if the carbon deposition occurs at a rate higher than carbon gasification, the catalyst is deactivated.

Unfortunately, there is a lot of research that needs to be undertaken, as neither of the reforming mechanisms is fully understood. Uncertainties lie in the coke formation mechanism and its interactions with tars for reforming. For example, both increases and decreases in catalytic activity have been associated to coke deposition [107,110]. Moreover, the effect of the migration of metals in the char structure could lead to different behaviours and needs further analysis.

3.2. Reforming kinetics

Using data from experimental observation, chemical kinetics are used to represent the changes in concentration of the chemical species. Due to the complexity of tars, authors often utilize simplified kinetics, with employed methodologies classified as lump and model compound models [15,121]. When the lump methodology is used, the tar species are considered as a mixture of tars, ignoring species specific characteristics. On the other hand, model compound models use species representative of a certain type of tar, with the most commonly used being naphthalene to represent PAHs, toluene as a representative alkylbenzenes and benzene as an intermediate species [79,122].

The activation energies reported in some works employing char as catalyst for reforming lumps and model compounds are found in Table 4. In addition to regular chars, some chars impregnated with metal catalysts are included in the table for comparison purposes. With regards to regular chars, the trend shows that activation energies are lower when the SSA is higher. While the activation energy for reforming naphthalene using pine wood char from reference [123] appears to be lower than that of that calculated using coconut char [25], this is owed to a higher pre-exponential factor (i.e. higher minimum conversion) obtained from the coconut char. Generally speaking, the activation energies for naphthalene decomposition are the lowest of any extensively used model compound and are generally lower than those reported for lump models. Activation energies of lump models are higher due to the mixture of species in the lump. Additionally, as seen in Table 4, the activation energies for the lump models using chars impregnated with metals are much lower than those using char, demonstrating their superior activity. However, metal catalysts have an economical shortcoming. On the other hand, there is a variability in the

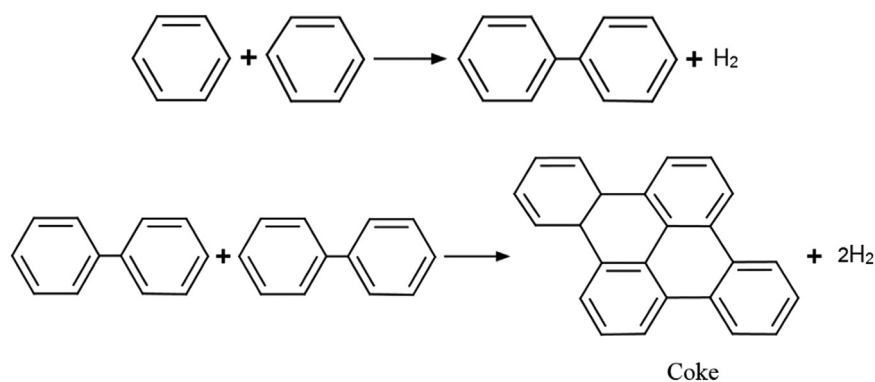


Fig. 7. Simplified mechanism of coke formation from benzene [115].

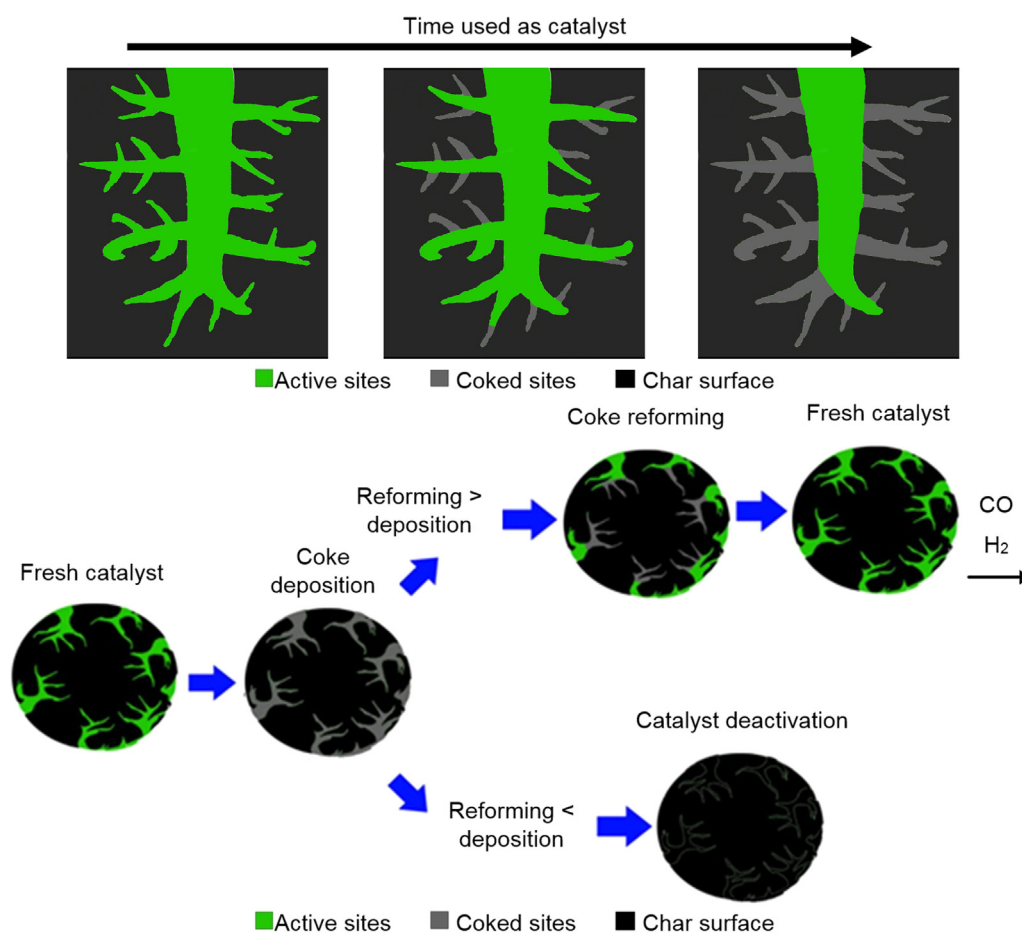


Fig. 8. Illustration of the coke deposited in the pores present in the surface of the char catalyst. a) Shows the progression of pore coking starting with micropores and b) shows the processes of coke gasification and catalyst deactivation due to coking.

parameters reported in the lump studies with activated chars, possibly associated to differences in the tar composition.

Fig. 9A and B depict a plot of the rate constants using parameters from literature for reforming toluene and naphthalene, respectively. In Fig. 9B, the dry sewage sludge char performs much worse than the other chars; this is most likely associated to differences in the SSA of the chars [16,25,124], in accordance to high SSA favouring the adsorption and heterogeneous reforming of PAHs [118]. The dry sewage sludge char has a SSA of 55 m²/g compared to 331 m²/g in the pine bark char and 597 m²/g in the coconut char [16,25,124].

Importantly, the activation energies from the literature are apparent activation energies, that is, do not provide in-depth information of the energy required for the adsorption/desorption phenomena in the

reaction mechanism. No studies have been reported that include detailed surface kinetics. Instead, homogeneous models employing first order rate laws, where diffusion phenomena is neglected, are used [25,98,107,126–128].

3.3. Use of regular char as a catalyst

Results from different studies using char as a catalyst for tar reforming are summarized in Table 5. The activity of char has been compared with that of Ni, biomass ash, olivine, dolomite and silica sand [43]. At temperatures around 900 °C, the tar decomposition capabilities of char are almost equal to those of Ni, providing almost 100% conversion; moreover, char was also proven to be an effective catalyst to

Table 4

Activation energies and properties of char-based catalysts reported in literature. N/R: Not reported.

Tar species	Activation energy (kJ/mol)	Pre-exponential factor	Type of catalyst	Ultimate analysis				Specific surface area (m ² /g)	Particle size (mm)	Additional description	Ref.
				C	H	O	N				
Toluene	75	4.10×10^4	Coconut char	91.4	0.3	1.7	0.9	597	1–2.8	Commercial char	[25]
	88	9.50×10^4	Dry sewage sludge	18.1	0.5	0.0	1.1	55	2–2.8	Rich in ashes (84% wt.)	[25]
	90	2.60×10^5	Pine bark char	88.1	0.5	10.3	1.0	310–331	0.21–0.42	Pyrolysis char	[124]
Naphthalene	61	1.87×10^4	Pine wood char	87.9	0.6	6.4	0.3	330.4	0.5–0.8	Pyrolysis char	[123]
	72	5.30×10^4	Coconut char	91.4	0.3	1.7	0.9	597	1–2.8	Commercial char	[25]
	63	7.60×10^3	Dry sewage sludge	18.1	0.5	0.0	1.1	55	2–2.8	Rich in ashes (84% wt.)	[25]
Lump	57	1.32×10^6	Char impregnated with Ni	68.1	4.9	25.7	0.6	N/R	0.05–0.15	Ni load was 2.34% wt.	[106]
	61	2.11×10^6	Char impregnated with Fe	68.1	4.9	25.7	0.6	N/R	0.05–0.15	Fe load was 2.34% wt.	[106]
	82	5.39×10^6	Coal AC	68.1	4.9	25.7	0.6	N/R	0.05–0.15	Steam activation @ 800 °C for 10 min	[106]
	146	2.63×10^3	Mesquite AC	73.6	3.5	14.6	0.4	4.5	N/R	Commercial AC	[125]
	154	38.3×10^3	Commercial AC	91.2	0.12	1.18	0.6	1176	0.8	Activated with steam	[125]

degrade more stable tars than those produced from biomass, produced during the pyrolysis of plastics such as polyvinyl chloride [129]. In [128] and [34] experiments similar to those from [43] were conducted; a notable difference in conversion was found. This difference is associated to the reaction atmosphere. Char can undergo continuous site activation under CO₂ or steam, reforming the coke in the pores and contributing to the resilience of the catalyst. If the char catalyst is deactivated due to coke, H₂ can regenerate the surface, restoring the char activity and providing further advantages in terms of heating value with constraints placed in the economic feasibility of the process [130]. Interestingly, although it may increase the amount of oxygenated groups in the surface, even after coking, char treated with O₂ will exhibit a decrease in its reforming capabilities [108]. Additionally, there is a relationship between the pore sizes and the catalyst resilience. It has been found that while mesopores do not contribute as much as micropores to provide a high initial tar conversion, they are more resilient to coke and increase the lifespan of the catalyst [131].

Studies using chars with high ash contents (over 25% weight) as catalysts led to the discovery of interactions between the ashes and the tars. Bonds are formed between the tars and the inorganic species, facilitating tar adsorption and heterogeneous reforming [132].

Finally, the reforming conditions and the properties of the gas mixture to be reformed have an important effect in the solid-gas interactions. While the H₂ and CO produced are directly proportional to the reforming temperature, the CH₄ yield follows the opposite trend. Char has affinity for reforming the CH₄ produced from the decomposition of alkylbenzenes, increasing the H₂/CO ratio of the gas, which is useful for liquid fuel production [122,133].

3.4. Use of activated carbon as a catalyst

A variety of ACs, including and not limited to commercial AC, have been employed either as catalysts or support for tar reforming; a summary of the activation conditions can be found in Table 6. Char can be activated either physically with gasifying agents, where some of the pores are widened, or chemically with a solution to remove ashes in the surface, create acidic sites and increase the SSA. When compared to regular char, AC provides better tar conversions but similarly to regular char, AC deactivates during operation. From the observed products during catalytic reforming, it is inferred that the differences between the conversions obtained with AC and regular char arise not only from differences in surface area, but also from the different pore structures [45]. Arguably, this indicates a relationship between the molecular weight of tars, the pore size of chars and the reforming mechanism to be followed.

AC enhances the H₂ production by hydrocarbon cracking and carbon gasification reaction (Eqs. 1 and 8) aided by the presence of –H in the activated char surface [139]. Reactivity of activated char also depends on the type of activation. Chemical activation removes AAEM, leading to decreased interactions between the chars and the gases [135]. In terms of activated char, char activated with CO₂ presents more O-functional groups when compared to its counterpart activated with H₂O, leading to overall better activity. Further, spent char catalysts activated with CO₂ exhibit activity even after use, showing potential for subsequent uses [110]. As chemical activation generally results in a larger increase in SSA than physical activation [140], a comparison between chemically and physically activated char from the same precursor can be done to determine whether the AAEMs can be

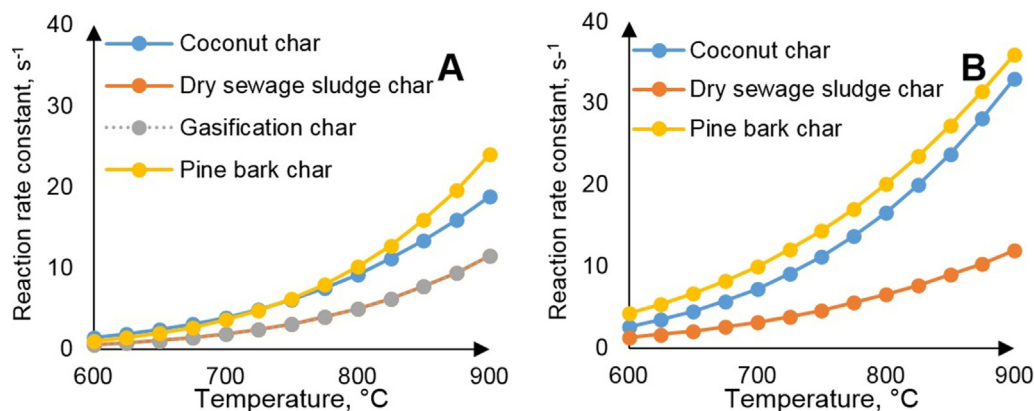


Fig. 9. Apparent reaction rate constants for reforming a) toluene and b) naphthalene reported in literature [16,25,106,124,126].

Table 5
Syngas composition with or without the use of a catalyst. N/A: Not reported.

Feedstock	Operating Temp. (°C)	Reforming agent	Reactor type	Catalyst	Composition					Composition					Ref.
					H ₂	CO	CO ₂	CH ₄	C ₂ -C ₃	H ₂	CO	CO ₂	CH ₄	C ₂ -C ₃	
Laboratory bio-oil	800	Steam	Fixed bed	Gasification char	50.74	17.83	21.19	10.24	–	65.91	14.08	18.33	1.68	–	[136]
Mallee wood	800	Steam/O ₂	Fixed bed	Mallee wood char	50.81	17.30	23.56	8.33	–	53.75	20.44	16.9	8.91	–	[102]
Wheat straw	800	Steam/O ₂	Fixed bed	Mallee wood char	48.60	15.86	27.51	8.03	–	53.28	17.96	20.37	8.39	–	[102]
Corn stalk	800	Steam/O ₂	Fixed bed	Mallee wood char	46.86	17.87	26.82	8.45	–	53.37	18.08	21.31	7.24	–	[102]
Wheat straw	900	N/A	Fixed bed	Wheat straw char	18.20	35.03	29.14	17.63	–	46.61	26.31	18.01	9.07	–	[135]
Wheat straw	900	N/A	Fixed bed	Rice husk char	18.20	35.03	29.14	17.63	–	42.34	22.37	23.69	11.60	–	[135]
Wheat straw	900	N/A	Fixed bed	Cotton stalk char	18.20	35.05	29.14	17.63	–	50.12	21.11	22.12	6.65	–	[135]
Subbituminous coal	650	N/A	Fixed bed	Subbituminous coal	48.94	17.02	10.02	22.57	1.45	43.56	17.52	9.40	26.77	2.75	[134]
Wood pellets	800	Steam	Fixed bed	Refuse derived fuel char	19.6	42.3	16.2	15.1	6.70	34.00	29.90	21.70	10.50	3.90	[112]
Wood pellets	800	Steam	Fixed bed	Date char	19.6	42.3	16.2	15.1	6.70	25.00	40.10	16.20	12.80	5.90	[112]
Wood pellets	800	Steam	Fixed bed	Tyre char	19.6	42.3	16.2	15.1	6.70	29.00	34.00	20.30	12.10	4.70	[112]
Wood pellets	800	Steam	Fixed bed	Acid washed tyre char	19.6	42.3	16.2	15.1	6.70	28.64	37.86	10.12	12.14	11.24	[127]

Table 6
Activation conditions of some of the activated char catalysts reported.

Precursor char	Activation method	Activating agent	Temperature	Activation Time	Ref.
Coal pyrolysis	Chemical	H ₂ O and KOH wash	800 °C	3 h	[137]
Spruce wood	Physical	CO ₂	800 °C	1.5 h	[53]
Red cedar	Chemical	N ₂ and KOH/NaOH wash	800 °C	1.5 h	[101]
Spruce wood	Physical	CO ₂ /N ₂ mixture	500 and 800 °C	1 h	[45]
Brown coal	Chemical	H ₂ O and H ₂ SO ₄ wash	800 °C	10 min	[64]
Hydroxymethyl cellulose	Physical	CO ₂	600, 700 and 800 °C	2 h	[138]

sacrificed to increase the SSA in AC.

3.5. Use of char/activated char as a catalyst support

In addition to being an attractive catalyst by itself, char has demonstrated interactions with tars when used as a support [106]. Preparation of the char catalysts is usually done by the impregnation method, described in Fig. 10 [141]. In this method, the chars are soaked with a solution containing metal ions which are adsorbed and finally oxidized with air to form metal oxides during the calcination step. During impregnation, since some of the pores are filled, the char loses some of its surface area and active sites. This effect is specially remarkable when using AC as a catalyst support [101]. Additionally, care has to be placed during calcination as under certain conditions, this step can lead to significant modifications in the char structure. For this reason, calcination may be skipped altogether when using pyrolysis chars [54]. Multiple species can be employed at the same time during impregnation leading to an overall increase in activity due to the combined catalytic activity of the metals [142]. However, the sequence of impregnation for catalyst synthesis has an important effect in performance, as every subsequent impregnation blocks additional pores in the support surface. This leads to diffusion limitations during impregnation, reflected in a reduced catalytic activity [143]. Moreover, the distribution of the ashes over the char surface is important for catalysis [46]: in the scenario where the support and the tars do not have adequate contact, less CO is formed and more CO₂ is favoured [50]. This also causes certain competition between the supported catalyst and the char, as when the supported metal is well distributed, the supported metal promotes the formation of H₂ while both the supported metal and the char promote the formation of CO.

Char can support a variety of metals. The most popularly employed are Fe and Ni [54,106,130,144,145], and K, Ca and Co are also utilized to some extent [143,146]. Fe catalysts supported by char also exhibit

potential for decomposition of NO_x precursor species [23]. In this situation, the H-radical yield from reforming reactions are converted to NH₃ by displacement reactions. Catalysts based on metal species can be reduced to their metallic state while undergoing tar reforming, giving place to the participation of the metal species in breaking the C-H and C-C bonds in the hydrocarbon [54]. Although char-supported metal catalysts normally perform better than pure char catalysts during reforming [46,106,147], they have shortcomings associated with their cost and possibly undesirable oxidation of the minerals in the catalyst, leading to changes in porosity and SSA [144].

4. Biomass gasification ashes for catalytic tar reforming

4.1. Uses of ashes as a catalyst

Popular mineral catalysts are dolomite, magnetite and olivine, composed mainly by Ca, Mg, Fe and Si, respectively [14]; all of the mentioned species may be present in ashes from gasification, as seen in Fig. 11 [34,67,97]. Although a minority of the gasification solid products, ashes have important effect in the catalytic activity for tar reforming. Alas, the use of ashes as a catalyst for tar reforming has been limited to a few investigations.

Fe and Ca (mostly found in coal and wood biomasses, respectively [47,59]) have demonstrated capabilities to reduce NO_x precursors and reform heavy tars [30,148]. Further, CaO and other species present in ashes (Al₂O₃, Fe₂O₃, MgO and K₂O₃) adsorb CO₂, shifting thermodynamic conditions to favour the decomposition of alkylbenzenes [122,133] and formation of H₂ [95,149,150], and may even prevent the formation of some tar species during gasification [151,152]. Moreover, adequate oxidation contributes to the development of pores and increases in the surface area of the char particles via the reverse Boudouard reaction (Eq. (9)), with inorganics further impacting reaction rates with cation exchange capacity. Since alkaline/alkaline earth

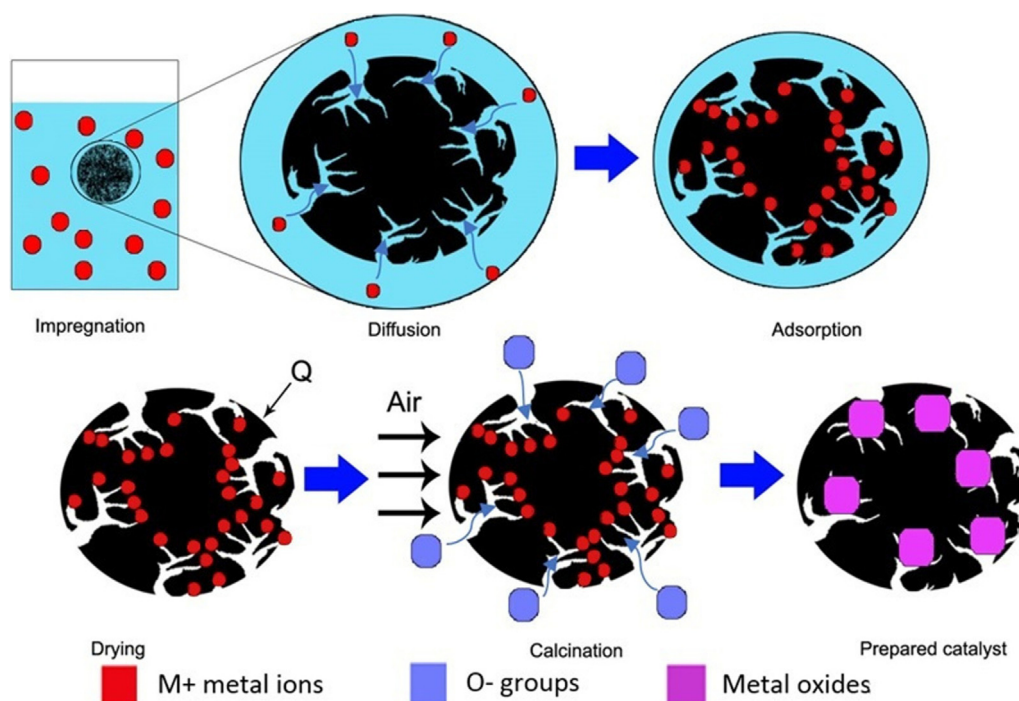


Fig. 10. Visual description of the impregnation method for catalyst preparation.

species constitute a large percentage of the ashes, these can be used for synthesis of catalysts [74]. In addition to increasing the overall LHV (Lower Heating Value) of the product fuels from conversion by decarboxylation and methanation reactions, ashes have proven to be valuable in reforming the catalyst-poisoning soot and favouring the degradation of pollutant-precursor HCN [23,32,153,154].

4.2. Uses of ashes as a catalyst support

Ashes as supports are not as effective as char for the reforming of tars but provide better thermal stability and may be cheaper. For example, in an experiment where rice husk chars and ashes were compared as supports for catalysts based in Ni, the ashes exhibited about double thermal stability when compared to char [54].

The most popular catalysts supported by ashes are Ni and Fe. Between the two, ashes with Ni have better activity when compared to ashes with Fe [99,100]. On another instance, ashes were tested as a support for Ni and compared with a commercial Ni/Al₂O₃ catalyst for tar reforming in a fixed-bed reactor. Both catalysts performed similarly, decomposing about 40% of the tars.

While the tar conversions provided by ashes are not particularly significant, catalysts based in ashes can be cheaply synthesized. The inorganic species in the ashes also are known to increase the activity of

metal catalysts for converting hydrocarbons, and favour the water gas-shift for inhibition of soot deposition and H₂ production [99,155]. Hence, further research to improve the activity of catalysts based in ashes will certainly pay off.

5. Concluding remarks

The utilization of chars, activated chars and ashes as catalysts and catalyst support for tar reforming was reviewed and analysed in this work.

Between char, activated char and ashes, the activated char shows the highest activity for reforming tars into CO and H₂, followed by regular char and finally ashes. However, char impregnated by nickel exhibits higher activity than pure char catalysts. The activities of the catalysts are associated to the surface area, pore size and presence of metallic species. The metallic species found in some solids can be valuable assets, as these have different positive secondary effects. For example the presence of Fe₂O₃ in char increases the number of catalytic active sites and provides capabilities for removing tars and additional pollutants such as the NO_x species. Therefore, it is important to assess whether the surface area of the presence of benevolent metallic/inorganic species in chars is better for clean up in a given case before deciding on a char activation methodology.

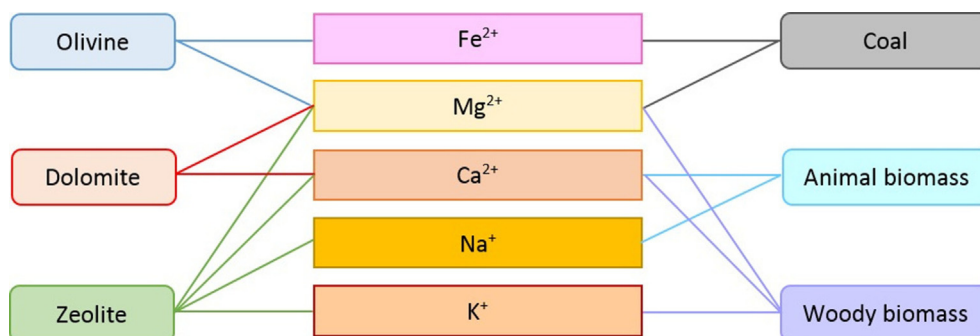


Fig. 11. Common inorganic species that are found both in popular mineral catalysts and biomasses.

While char-based catalysts appear promising and may be able to compete with commercial catalysts such as those based on nickel, there are a few aspects that could receive additional work for future technologies. For example, it appears that there is a relationship between the molecular weight of tars, the pore size of chars, the reforming temperatures and the reforming mechanism to be followed. It is known that heterogeneous reforming favours polyaromatic hydrocarbons at high temperatures, while light tars follow the homogeneous reforming mechanism. Hence, the ability of chars to selectively remove tar species can prove beneficial, as the less problematic tars can receive less intricate treatment or, depending on the application of the gas, be ignored altogether. Additionally, the interactions between tars and the O- and H-groups in the char surface require deeper exploration.

On the side of ashes, even if their tar reforming activity is not as high as that of the other studied catalysts, their thermal stability and notable capabilities to degrade undesirable substances other than tars such as HCN and H₂S make them interesting for syngas clean-up. The synergetic usage of ashes and chars in a multi-stage reactor could represent a viable alternative to produce quality syngas free of pollutants.

For the moment, the most conversion-effective char catalysts are to be those based in char impregnated by nickel, even if they are constrained economically. A major shortcoming for pure char catalysts lies in the fact that they appear to be resilient only at high temperatures (over 900 °C). However, some major advantages of the char-based catalysts include their continuous formation during gasification and their ease of disposal by gasifying the catalyst whenever it loses activity. Therefore, an adequate control of the coke reforming and coke deposition rate is a key aspect to achieve long operation times with raw char based catalysts and make them compete with nickel. Particularly, analysing the activity of chars with different porous structures using different gasifying agents at different temperatures may provide valuable information. This can ultimately lead to catalysts that provide a tar conversion efficiency as high as those obtained with Ni based catalyst to lower economic cost. In the end, this will translate to reductions of the cost of producing quality syngas, with the reduction of the costs associated to the handling of solid wastes, increasing the sustainability of the technology for fuel production.

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Declarations of interest

None.

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